# Methane Hydrate Formation Kinetics

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**Abstract**

Kinetic parameters for methane hydrate formation were obtained from film growth measurements at the methane-water interface. Experimental data were collected for methane hydrate formation over the pressure and temperature ranges of 3.55 to 9.06 MPa and 1.0 to 4.0 $^o$C, respectively. The growth rate was found to be proportional to the supercooling, which indicates that crystallization proceeds by a continuous growth mechanism. A model for hydrate formation was proposed, which accounts for both heat transfer and kinetics. Molecular attachment kinetics were assumed to follow Arrhenius behavior, and the heat transfer coefficient was assumed constant. The heat transfer assumption was verified using a thin wire approximation, which was considered a geometrical analog. The resulting parameters were regressed and an activation energy of 171 kJ/mol, a frequency factor of 1.605 x $10^{36}$ W/m$^2$ K, and a heat transfer coefficient of 42,325 W/m$^2$ K were found.

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**Introduction**

Natural gas hydrates constitute earth's largest natural energy resource, plug offshore oil and gas production pipelines, and have been studied as a major factor in sequestering $CO_2$ in deep oceans. It follows that the kinetics of natural gas hydrate formation is of great industrial and environmental interest.

Gas hydrates are inclusion compounds comprised of approximately 85 mole % water, 15 mole % guest, and thermodynamically stable at low temperatures and high pressures. The large concentration of both guest and host molecules in the hydrate phase, which is much greater than the bulk phase solubility of either constituent, results in crystal growth at the gas-liquid interface.

Several studies of interfacial hydrate formation have recently appeared in the literature [1-3]. Optical experiments performed by Sugaya and Mori [1] revealed that initial hydrate growth occurs as a thin film propagating across the guest-water interface, and further growth or dissociation is controlled by mass transfer through the film or in either bulk phase. Uchida et al. [3] observed hydrate film growth at both the gas and liquid $CO_2$-water interface, and measured hydrate film propagation using optical microscopy.

The purpose of this research was to extend studies of hydrate formation at the gas-liquid interface, and determine the growth rate response to perturbations in the temperature driving force, $\Delta T$, defined as the three-phase equilibrium temperature, $T_{eq}$, minus the bulk fluid temperature, $T_{bulk}$. This goal was accomplished using optical microscopy to experimentally measure the rate of methane hydrate film propagation across the methane-water interface. The growth rate response to driving force perturbations as well as

observations of crystal morphology was used to identify a possible mechanism for molecular attachment. Modeling of film growth rates was performed to determine intrinsic rate parameters as well as heat transfer from the advancing hydrate interface.

**Experimental Details**

*Apparatus*

This work introduces a simple technique to measure kinetics of methane hydrate formation at the gas-liquid interface using optical microscopy in a high pressure visual cell. The cell, shown in Figure 1, is constructed of three brass plates. The middle plate contains a 5ml Teflon sample chamber that is bound on either side by sapphire windows. The two outer plates seal the sample chamber and resist a maximum internal pressure of 9.06 MPa. A Neslab RTE-220 cooler was used to circulate coolant through ports machined into the cell to maintain a constant cell temperature. The cell is encased in a Textilite insulating block, which ensures temperature stability, and an Omega RTD was placed into a 0.32 cm well drilled into the body of the cell to monitor the temperature to within $\pm$ 0.3 $^{\circ}$C. Gas is supplied to the cell through a small injection port and the pressure is monitored using a Heise pressure gauge with an accuracy of 34.5 kPa.

The contents of the cell were monitored using a Sony CCD camera with an Olympus SZ60 microscope. The experiments were recorded using a Sony SLV-R1000 VCR and ImagePro$^{©}$ image analysis software was used to measure spatial advancement of the hydrate film at consecutive time intervals. The uncertainty of the spatial measurement and time interval were 5 $\mu$m and 1/30 second, respectively. Calibration of the image analysis software was performed using standard 100 $\mu$m spheres purchased from Duke

Scientific Corporation.

*Procedure*

The sample chamber was filled with 1.5 g of deionized water at room temperature and atmospheric pressure. After the cell equilibrated to the experimental temperature, which ranged from 1 $^{\circ}$C to 4 $^{\circ}$C, the sample chamber was pressurized with research grade (99.92%) methane obtained from General Air, Denver. Experimental pressures ranged from 3.55 MPa to 9.06 MPa. Initial hydrate formation was observed stochastic, however, subsequent hydrate formation usually occurred within one hour of pressurization. Each experiment was recorded and images were later captured at 0.5, 1.0, or 5.0 second time intervals using single frame advancement. The time interval was chosen to ensure collection of several data points and spatial measurements larger than the calibration unit, which depended on the growth rate. Captured images were then converted into a sequence, which allowed spatial measurements of film progression from an arbitrary point at known time intervals. Derivatives of distance versus time plots, which were all linear with $R^2$ values (correlation coefficient) greater than 0.99, yielded the velocity of the progressing hydrate front.

**Results and Discussion**

*Features of Methane Hydrate Film Growth*

Tiller [4] describes two primary crystal growth mechanisms that depend upon the interfacial driving force: step and continuous growth. At low and moderate interfacial driving forces crystallization proceeds by molecular attachment at step kink sites and the solid interface advances only by the lateral movement of steps. At high driving forces growth proceeds normal to the interface by a continuous mechanism. In this case, the solid

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interface roughens and molecules can attach anywhere on the surface. In this study both mechanisms were observed, however, all growth rate measurements were conducted in the continuous regime.

Methane hydrate single crystals formed at the methane-water interface are shown in Figure 2a. Cahn et al. [5] report that development of well defined crystallographic surfaces (single crystals) implies that growth must proceed by a step mechanism. Increasing the pressure, however, results in a transition from step to continuous growth as shown in Figure 2b. The transition occurred at a temperature driving force of approximately 0.4 $^o$C.

In the continuous regime growth facets disappear and the film roughens. Figure 3 shows a methane hydrate film propagating across the interface. This image was captured normal to the methane-water interface, and the hydrate film was distinguished by the intensity of reflected light relative to the dark continuous water phase. The disparity in reflected light intensity from the film surface indicates a rough topography. The film thickness remained constant at the solidification interface indicating that mass transfer is limited perpendicular to the methane-water interface.

*Measurements of Hydrate Growth Rates*

Methane hydrate film growth rates were measured at pressures ranging from 3.55–9.06 MPa at three bulk temperatures; 1.0 $^o$C, 2.0 $^o$C, and 4.0 $^o$C. The results of these experiments are summarized in Table 1. The equilibrium temperature was calculated at the system pressure using the Multiflash$^©$ 2.9.10 hydrate prediction program. Figure 4 shows the growth rates as a function of the bulk temperature for different hydrate equilibrium temperatures. Regression analyses of each series, shown as solid lines, indicate that the

growth rate has a linear dependence with bulk temperature at constant equilibrium

temperatures.   Cahn et al. [5] report that growth rates linear in supercooling constitute

strong evidence for continuous growth.   This analysis, however, is only valid at constant

equilibrium temperatures, which results from dependence of the absolute interface

temperature on molecular attachment kinetics.    A cross plot of these data, Figure 5, shows

that the growth rates are nonlinearly dependent with equilibrium temperature at constant

bulk temperatures. The dependency differences of the equilibrium and bulk temperatures on

the growth rate were a major and unexpected result of this work, and indicate ambiguity in

the defined driving force.  The results indicate that a unique growth rate may not exist for a

given driving force, and that both the bulk and equilibrium temperatures must be specified

to adequately define molecular attachment at the hydrate interface.

*Modeling Hydrate Kinetics*

Along the advancing front mass transfer is assumed negligible and heat transfer

dominates.  Heat transfer is typically a controlling process in crystallization phenomena.  In

fact, with fast interface attachment kinetics, growth rates have been observed proportional

to $t^{-1/2}$, which is the relationship predicted using conduction alone [6].  It is possible,

however, to have sluggish interface attachment kinetics, which would result in growth rates

slower than model predictions and a different time dependence.  Considering this, it is

appropriate to compare experimentally and theoretically determined growth rates using a

moving boundary model.   Figure 6 is a simplified illustration of hydrate growth at the

methane-water interface.  The hydrate film is depicted as moving parallel to the methane-

water interface with the *x*-direction normal to the moving boundary, *X(t)*.   The temperature

at the moving boundary must be the hydrate equilibrium temperature at the system

pressure, and it is assumed that no temperature gradient exists within the hydrate phase. Complete wetting of the hydrate film is assumed, which is consistent with observations by Hirata and Mori [7]. The bulk water is initially at the system temperature, $T_{bulk}$. The one-dimensional energy equation is given by

$$\frac{\partial T}{\partial t} + V_x \frac{\partial T}{\partial x} = \alpha_w \frac{\partial^2 T}{\partial x^2} \tag{1}$$

with initial and boundary conditions of

$$T(0, x) = T_{bulk} \tag{2}$$

$$T(t, X(t)) = T_{eq} \tag{3}$$

$$-k_w \frac{\partial T(t, X(t))}{\partial x} = \rho_H \lambda_H \frac{dX}{dt} \tag{4}$$

where $T$ is the temperature in the bulk water phase, $V_x$ is the fluid velocity in the $x$-direction, $\alpha_w$ is the thermal diffusivity of water, $\rho_w$ is the density of water, $\lambda_H$ is the heat of hydrate dissociation, dX/dt is the velocity of the moving interface, and $k_w$ is the thermal conductivity of water. The velocity of the fluid in the $x$-direction results from density changes at the moving boundary, which is found using jump conditions [8] at the interface and is given by

$$V_x = \left( \frac{\rho_w - \rho_H}{\rho_H} \right) \frac{dX}{dt} \tag{5}$$

where $\rho_H$ is the hydrate density. This problem yields an analytical solution for the velocity of the moving boundary given by

$$\frac{dX}{dt} = \chi \sqrt{\frac{\alpha_w}{t}} \tag{6}$$

where $x$ is the root of the following transcendental equation:

$$x \, erfc\left(x\frac{r_H}{r_W}\right)\exp\left(x\frac{r_H}{r_W}\right) = \frac{k_W\left(T_{eq}-T_{bulk}\right)}{r_H l_H a_w\sqrt{p}}$$ (7)

A comparison of predicted and experimental growth rates is shown in Figure 7. The large disparity between these results coupled with constant growth rates indicates that additional heat transfer occurs through convection.

Free convection at the moving boundary can occur through two mechanisms; bouyancy driven flows and thermocapillary convection. Tiller [6] contends that although both forms of free convection may occur thermocapillary convection will dominate in small systems; a contention that has been experimentally demonstrated for systems of water with a free boundary [9].

Convection at the moving boundary can be modeled only if both the geometry and the hydrodynamics of the system are known. The exact geometry of the hydrate interface is unknown; however, approximations can be made by analyzing systems with similar geometry. A unique and important characteristic of the moving interface is that it is very thin [10]. In this limit the surface area to volume ratio becomes very large and the most applicable approximation would be that of a thin wire. Kurdyumov and Fernádez [11] solved the full Navier-Stokes and energy equations numerically for forced convection about a circular cylinder at low Reynolds numbers, which resulted in a correlation valid for Reynolds numbers below a critical value (point of boundary layer separation) and Prandtl numbers equal to or greater than order unity.

Sensitivity analyses of Nusselt numbers calculated using this correlation indicate that the heat transfer coefficient is a strong function of cylinder radius and a small function

of Reynolds number. Analogously, heat transfer from the hydrate surface should be very sensitive to the film thickness and relatively invariant with hydrodynamic changes. If the film thickness changes very little with driving force than a constant heat transfer coefficient is expected.

Our model combines convective heat transfer and interfacial growth kinetics resulting in transport independent rate parameters. The foundation of this model is derived from an energy balance at the moving boundary, which implies that the convective heat transfer cannot exceed heat generated at the moving interface. It is possible, however, to have growth kinetics that are sluggish relative to heat transport. Considering this, an overall rate constant is defined accounting for both kinetic and heat transfer resistance, and is given as:

$$\mathbf{l}_H \, \mathbf{r}_H \, \frac{dX}{dt} = K \, (T_{eq} - T_{bulk}) \tag{8}$$

$$\frac{1}{K} = \frac{1}{k} + \frac{1}{h} \tag{9}$$

where $K$ is the total resistance, $h$ is the heat transfer coefficient, and $k$ is the methane hydrate kinetic rate coefficient.

In regard to the thin wire approximation for heat transfer it is reasonable to assume a constant heat transfer coefficient. The kinetic rate coefficient is proposed to follow an Arrhenius type expression given by

$$k = k_o \exp\left(\frac{-E_a}{R} \frac{1}{T_{eq}}\right) \tag{10}$$

where $k$ is the rate constant, $k_o$ is the frequency factor, and $E_a$ is the activation energy. The

resulting model has three unknown parameters, which were regressed from the data using a

least-squares method.  Values for the regressed parameters are given in Table 2.  The heat

transfer coefficient agrees well with values calculated using the thin wire approximation for

a film thickness and Reynolds number ranging from 2 μm to 5 μm and $10^{-5}$ to $10^{-2}$,

respectively.  The film thickness range compares well with the value of 5 μm reported by

Makogon et al. [12] for methane hydrate films.  The activation energy was found to be 171

kJ/mol, which is larger than values reported by Mullin [13] for diffusion (10-20 kJ/mol)

and surface integration (40-60 kJ/mol).  The order of magnitude disparity between the

regressed and diffusion values suggests that hydrate formation is surface integration

controlled.  The large regressed activation energy may result from complexity of the

ordering process at the interface, which becomes more favorable at higher temperatures.  At

the solidification interface both methane and water molecules must combine to form the

stable hydrate lattice.  It is reasonable to assume that an increase in the temperature at that

interface results in an increased probability of molecular attachment, which is supported by

the experimental data.

Figure 8 shows a comparison of model predictions using regressed parameters

given in Table 2 with experimental data.   The predictions are in very good agreement with

the experimental data, and deviations are attributed to the heat transfer approximation.  It is

important to note that both $T_{eq}$ and $T_{bulk}$ are required for this calculation, and specification

of only $DT$ may result in erroneous growth rate predictions.  This behavior arises from the

kinetics of hydrate formation, which follow an Arrhenius type expression and depend

heavily on the temperature at the interface.

**Conclusions**

This study has established a technique to study the growth rates of methane hydrate films at the methane-water interface using optical microscopy. The results of this work indicate that molecular attachment at the hydrate interface is a stronger function of the equilibrium temperature than bulk temperature. It has also been determined that growth proceeds by a continuous mechanism as indicated by the growth response to bulk temperature perturbations at constant equilibrium temperatures and morphological features of the hydrate film. It should be noted that the same dependencies might not apply for methane hydrate single crystals [2]. It is reasonable to assume, however, that this technique could be extended using other pure guest molecules and multicomponent mixtures.

Conductive heat transfer was modeled and the solution to the moving boundary problem yielded growth rates of order magnitude smaller than experimentally determined growth rates. This analysis proved that heat transfer was dominated by convection. A model was proposed that combined interfacial attachment kinetics with convective heat transfer. The kinetic dependence was assumed to follow an Arrhenius expression and the heat transfer coefficient was assumed constant. The heat transfer assumption was verified by considering heat transfer from a thin wire, which was approximated as a geometrical analog to the thin film moving boundary. The regressed parameters were in reasonable agreement with values reported for typical crystallization, and predictions fit the data well. Deviations were attributed to the heat transfer approximation.

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Table 1
Experimetnally Determined Methane Hydrate Growth Rates

| P (Mpa) | $T_{eq}$ ($^{o}$C) | $T_{bulk}$ ($^{o}$C) | $\Delta T$ ($^{o}$C) | dX/dt (µm/s) | dX/dt[1] (µm/s) |
|---------|---------|---------|---------|---------|---------|
| 3.55 | 2.96 | 1.0 | 1.963 | 21.03 | 24.24 |
| 4.93 | 6.28 | 1.0 | 5.281 | 156.41 | 141.45 |
| 6.31 | 8.70 | 1.0 | 7.703 | 327.91 | 320.77 |
| 7.69 | 10.58 | 1.0 | 9.586 | 509.78 | 501.58 |
| 9.06 | 12.11 | 1.0 | 11.11 | 690.42 | 692.36 |
| 4.93 | 6.28 | 2.0 | 4.281 | 132.39 | 117.31 |
| 5.62 | 7.57 | 2.0 | 5.576 | 179.32 | 196.27 |
| 6.31 | 8.70 | 2.0 | 6.703 | 288.85 | 292.04 |
| 7.69 | 10.58 | 2.0 | 8.586 | 450.79 | 486.62 |
| 9.06 | 12.11 | 2.0 | 10.11 | 664.24 | 641.93 |
| 4.93 | 6.28 | 4.0 | 2.281 | 45.501 | 50.57 |
| 5.62 | 7.57 | 4.0 | 3.576 | 98.178 | 102.27 |
| 6.31 | 8.70 | 4.0 | 4.703 | 165.14 | 171.89 |
| 7.69 | 10.58 | 4.0 | 6.586 | 324.64 | 325.03 |
| 9.06 | 12.11 | 4.0 | 8.11 | 472.98 | 479.01 |

[1] Repeated experimental growth rates

Table 2
Model Parameters

| Parameter | $k_o$ (W/m$^2$ K) | $E_A$ (kJ/mol) | h (W/m$^2$ K) |
|---------|---------|---------|---------|
| Regressed Value | 1.60567e36 | 20599 | 42,326 |

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Figure Captions


Figure 1.    High Pressure Visual Cell.

Figure 2a.   Methane Hydrate Single Crystals at the Methane-Water Interface at 3.2 MPa and 1.0 $^{\circ}$C.

Figure 2b.   Transition from Step to Continuous Growth at 3.41 MPa and 1.0 oC.

Figure 3.     Methane Hydrate Film Propagating Across the Methane Water Interface

Figure 4.     Methane Hydrate Film Growth Rates as a Function of Equilibrium Temperature.

Figure 5.     Methane Hydrate Film Growth Rates as a Function of Bulk Temperature.

Figure 6.     Illustration of Hydrate Film Growth at the Gas-Liquid Interface.

Figure 7.     Moving Boundary Model Prediction.

Figure 8.     Combined Convection and Kinetic Growth Rate Model Predictions.

Teflon Ring

Insulating Block

Top Brass Plate

Central Brass Plate

5ml Sample Chamber

Gas Inlet

Thermocouple
Insertion Well

Bottom Brass Plate

Channel for Coolant

Sapphire Window

100 μm

Legend:
- $T_{eq} = 6.28\ ^{o}C$
- $T_{eq} = 8.70\ ^{o}C$
- $T_{eq} = 10.6\ ^{o}C$
- $T_{eq} = 12.1\ ^{o}C$
- Trendline

y-axis: $dX/dt\ (\mu m/second)$

x-axis: $T_{bulk}\ (^{o}C)$

Gas Phase

$T = T_{eq}$

Hydrate Film

Liquid Phase

$T = T_{bulk}$

$x = X(t)$

x